# Ceramic Films from Aqueous Solutions: *Engineering the Substrate*

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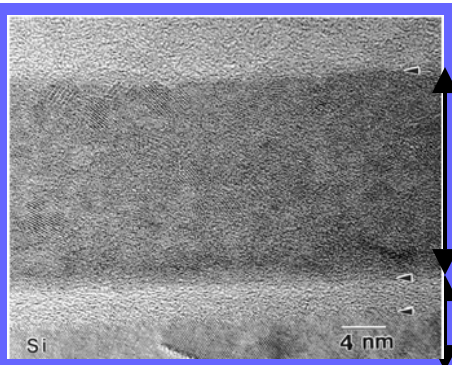
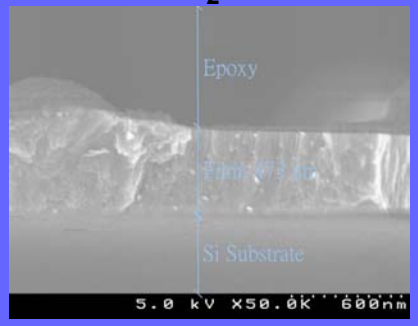
- ***Sulfonate*** ($-SO_3H$) surfaces
  - Strongly ***negatively*** charged ($-SO_3H \rightarrow -SO_3^- + H^+$)
  - $\Rightarrow$ nanocrystalline ***$TiO_2$, $ZrO_2$, $SnO_2$*** films
- ***Amine*** ($-NH_2$) surfaces
  - ***Positively*** charged ($-NH_2 + H_2O \rightarrow NH_3^+ + OH^-$)
  - ***Charge reversal*** in ionic double layer
  - $\Rightarrow$ ***$TiO_2$*** and ***$V_2O_5 \cdot nH_2O$*** films
- ***Alkyl ammonium salt*** ($-NR_3^+$) surfa
  - Strongly ***positively*** charged
  - $\Rightarrow$ 80-μm thick ***$V_2O_5 \cdot nH_2O$*** films

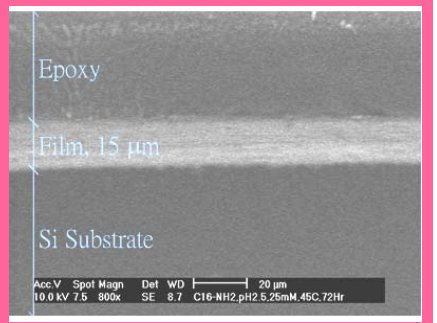


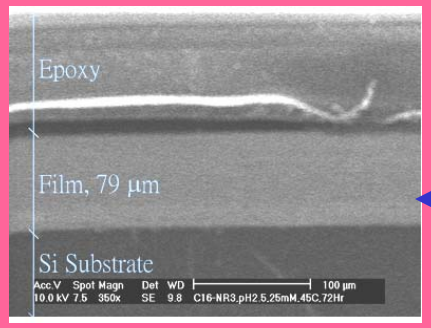

**25-nm $TiO_2$ film**

**Si w/-$SO_3H$ surface**

**470-nm $TiO_2$ film on Si w/-$NH_2$ surface**




**$V_2O_5 \cdot nH_2O$ films on Si with -$NH_2$ (above) and -$NR_3^+$ (left) surfaces**

This research focuses on forming crystalline films of functional oxides from aqueous media. Inspired by biological processes that produce mineral materials with outstanding properties at ambient temperatures from aqueous solutions, this approach offers lower-cost, environmentally more benign, and more versatile deposition of ceramic films than vapor or sol-gel routes.

Research at CWRU in this area has focused on engineering the substrate — in particular, using self-assembled organic monolayers (SAMs) to alter the surface chemistry — as a way to promote film growth. This provides unique insights that cannot be gained from the more common approach of studying solution chemistry alone (pH, temperature, concentration).

For example, sulfonate, amine, and alkyl ammonium salt surfaces span a wide range of surface charge density in aqueous environments. Sulfonated surfaces, which are strongly negatively charged at most pH values, promote deposition of films of positively charged colloidal oxides such as titania (shown here), zirconia, and tin oxide. At the other extreme, alkyl ammonium salt surfaces, which are strongly positively charged at most pH values, promote deposition of vanadium oxide films. (Aqueous vanadium complexes and colloidal vanadium oxide particles are negatively charged.) Amine SAMs, intermediate surfaces with moderate and highly pH-dependent positive charge, allow deposition not only of vanadia films, but also of titania films via the presence of a Stern layer (charge reversal zone) in the solution adjacent to the surface. This unexpected result, supported by recent AFM measurements, has important implications for deposition of functional oxide films. It may also shed new light on the role of amino acids in biomineralzation processes.